Electronic Supporting Information (ESI)

Figure S1
Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of 10 mgL$^{-1}$ morpholine in pH 10 carbonate buffer solution recorded using SPGE. Scan rate: 50 mVs$^{-1}$ vs Ag/AgCl

![Graph showing cyclic voltammetry responses](image1)

Figure S2
Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of 10 mgL$^{-1}$ morpholine in pH 10 carbonate buffer solution recorded using BDDE. Scan rate: 50 mVs$^{-1}$ vs SCE

![Graph showing cyclic voltammetry responses](image2)
**Figure S3**

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of 10 mgL\(^{-1}\) morpholine in pH 10 carbonate buffer solution recorded using GCE. Scan rate: 50 mVs\(^{-1}\) vs SCE

![Graph showing cyclic voltammetry responses](image)

**Figure S4**

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of 10 mgL\(^{-1}\) morpholine in pH 10 carbonate buffer solution recorded using AuE. Scan rate: 50 mVs\(^{-1}\) vs SCE

![Graph showing cyclic voltammetry responses](image)
**Figure S5**

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of 10 mgL$^{-1}$ cyclohexylamine in pH 10 carbonate buffer solution recorded using SPGE. Scan rate: 50 mVs$^{-1}$ vs Ag/AgCl

![Graph](image1)

**Figure S6**

Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of 10 mgL$^{-1}$ cyclohexylamine in pH 10 carbonate buffer solution recorded using BDDE. Scan rate: 50 mVs$^{-1}$ vs SCE

![Graph](image2)
**Figure S7**
Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of 10 mgL⁻¹ cyclohexylamine in pH 10 carbonate buffer solution recorded using GCE. Scan rate: 50 mVs⁻¹ vs SCE

![Graph S7](image)

**Figure S8**
Typical cyclic voltammetric responses in the absence (solid line) and presence (dashed line) of 10 mgL⁻¹ cyclohexylamine in pH 10 carbonate buffer solution recorded using AuE. Scan rate: 50 mVs⁻¹ vs SCE

![Graph S8](image)
**pH study of the mediators**

The plots of reduction peak potential $E_p$ vs. pH for the mediators N-(4-Amino-2-Methyl-Phenyl)-Benzenesulfonamide and N,N’-(1,4-phenylene)dibenzenesulfonamide are shown in figure S9 and S10 respectively. In case of N-(4-Amino-2-Methyl-Phenyl)-Benzenesulfonamide (S9) the plot shows a linear range with a gradient of 0.055 ($E/V = -0.055 + 0.444 \, E/pH \, R^2 = 0.98$). In case of N,N’-(1,4-phenylene)dibenzenesulfonamide (S10) the plot shows a linear range with a gradient of 0.060 ($E/V = -0.060 + 0.651 \, E/pH \, R^2 = 0.99$). Such a value is close to that expected for 2 protons and 2 electrons process according to the electrochemical step (1) of the proposed mechanism (see Scheme 1) (59 mV per pH unit at 25 °C) as deduced from the following equation:

$$ E = E^0 - 0.059 \frac{m}{n} \, pH \quad (11) $$

where $E^0$ is the standard reduction potential, $m$ and $n$ are the number of protons and electrons participate in the reaction respectively and the other symbols have their usual meaning.
Figure S9
Cyclic voltammetric responses obtained in carbonated buffer solution at different pH values. Plot of peak potential, $E_p$, as a function of pH for the electrochemical reduction of 100 μg mL⁻¹ N-(4-Amino-2-Methyl-Phenyl)-Benzenesulfonamide in carbonated buffer solution at different pH values. In all cases SPEs were utilised. Scan rate: 50 mV s⁻¹ vs. Ag/AgCl.

![Figure S9](image1.png)

Figure S10
Cyclic voltammetric responses obtained in carbonated buffer solution at different pH values. Plot of peak potential, $E_p$, as a function of pH for the electrochemical reduction of 100 μg mL⁻¹ N,N’-(1,4-phenylene)dibenzencesulfonamide in carbonated buffer solution at different pH values. In all cases SPGEs were utilised. Scan rate: 50 mV s⁻¹ vs. Ag/AgCl.

![Figure S10](image2.png)